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13. ABSTRACT (Maximum 200 words)

This research has investigated the growth of diamond films in the combustion flame of an oxyacetylene torch. As a result of this research we now have a good understanding of the parameters that affect the growth of high quality diamond films and a better understanding of the nucleation process. Research resulting in the growth of highly textured, high quality diamond films on Si(100) substrates is reported.

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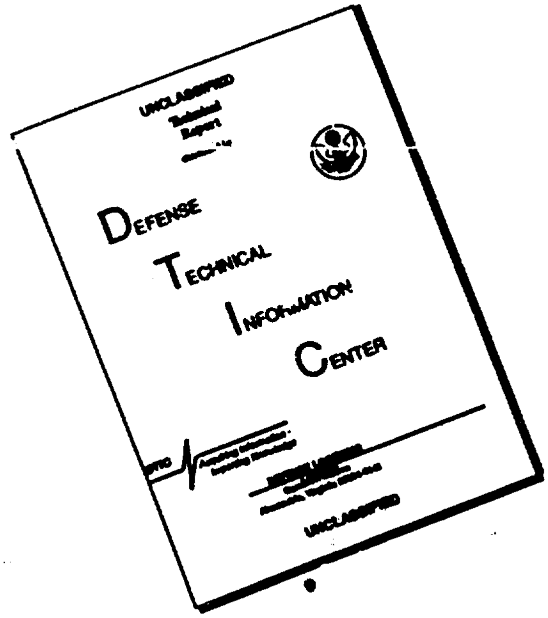

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CHARACTERIZATION OF DIAMOND FILM GROWTH IN A COMBUSTION FLAME

FINAL REPORT

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June 7, 1993

Summary: This research has investigated the growth of diamond films in the combustion flame of an oxyacetylene torch. As a result of this research we now have a good understanding of the parameters that affect the growth of high quality diamond films and a better understanding of the nucleation process. Research resulting in the growth of highly textured, high quality diamond films on Si (100) substrates is reported.

PROGRAM ACCOMPLISHMENTS

At the start of the program the combustion synthesis approach to diamond growth was in its infancy. Dr. Hirose (Nippon Institute of Technology - Japan) had just announced the feasibility of growing diamond films in a combustion flame and several programs around the world were just beginning to duplicate his results. The North Carolina State University program benefitted greatly by having Dr. Hirose spend a one-year sabbatical as a visiting Professor at NCSU in 1989-90. Under his expert guidance a combustion growth apparatus was quickly assembled, baseline deposition techniques established and the microstructure of baseline diamond films characterized. Real-time control over the acetylene combustion flame apparatus has since been achieved. A second system has been assembled within a controlled atmosphere chamber to permit future investigations to be conducted under inert or low pressure conditions.

This 3-year program has resulted in a number of important insights:

- The optimum parameters for growing high quality diamond films have been found to be: substrate temperature 600-750°C, O_2/C_2H_2 ratio of .95-.98, and a growth rate of about 30 μm/h. Deposition on substrates held at temperature below 900°C favor film growth with (111) surface facets; growth above 950°C favor films with (100) facets. The periodic shift to oxygen-rich (etching) conditions, O_2/C_2H_2 ratio of 1.01, leads to further improvements in film quality, eg. the Raman spectra indicates a decrease in the sp2 component (1530 cm^{-1} peak), see Figure 1. Diamond deposited under optimum combustion conditions have low conductivities rivaling those of natural diamond, see Figure 2. These conductivities fall considerably below those of films prepared by other low-pressure CVD approaches.

- Defect structures in diamond films have been found to display a strong substrate temperature dependence. At substrate temperatures below 500°C a high density of microtwinning is observed. Above 600°C the microtwinning is no longer observed and the overall defect density is drastically reduced. Stacking faults and dislocations are present, but in much lower concentrations. This suggests that enhanced surface diffusion at higher temperatures is sufficient to correct the stacking errors responsible for the formation of microtwins during growth. These findings upset the conventional wisdom on the growth of defect-free diamond films. Prior to our studies it had been felt that low defect films would result only above 950°C, where the growth surface shifted from (111) to (100).

- It has been found that film nucleation can be greatly enhanced by adjusting the flame chemistry during the first few minutes of the deposition experiment. Flame deposition parameters that increased carbon flux to the surface while suppressing oxide growth favor diamond nucleation. Interestingly, the spatial variation in diamond film growth rate across the flame diameter, which is frequently reported in the early combustion growth literature, has been found to be a nucleation kinetics issue. Once nucleated, nearly uniform film growth occurs over the entire cross section of the flame.

- The nucleation of diamond in a combustion flame can be greatly enhanced by surface treatments that increase surface roughness (e.g. surface scratching or grooving) and reduce initial oxide thickness (e.g. HF chemical etching). Nucleation of diamond at microcrystalline graphite and at soot particles has been observed. The mechanism is not presently understood in any detail.

- Nucleation of diamond is effectively stopped if an oxide thicker than about 50 Å covers the surface. Thus, we have demonstrated that selected area deposition of diamond is possible by patterning the substrate beforehand with SiO_2. In addition, by excluding O_2 from the ambient environment we have recently shown that flame scanning techniques can be employed to coat large areas. The exclusion of ambient O_2 provides much of the motivation for moving the experimental system into a controlled atmosphere chamber.

- Relatively well textured and smooth surfaces have been grown starting with pretreated surfaces that provided a high density of nuclei with direct registry to the Si (100) substrate. Near-continuous diamond films have been grown in a combustion flame using either a "mosaic" (oriented diamond-seeded) substrate supplied by M. Geis (1) or microwave pretreated surfaces (2), see Figure 3. Details of the pretreatment experiments are given elsewhere (2-5). The texture of the original diamond seeds has been maintained during the growth phase and nearly seemless coalescence of adjoining grains can be observed in both cases. Recently, very similar successes have been realized using Ni substrates. Whether similar in-situ pretreatment approaches can be developed for the combustion flame system will be the topic of the follow-on proposal.

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PROGRAM PUBLICATIONS:

- G. -H. M. Ma, Y. Hirose, S. Amanuma, M. McClure, J.T. Prater and J.T. Glass; "Microstructural Studies by TEM of Diamond Films Grown by Combustion Flame", accepted for publication in the Proceedings of the 2nd International Conference on New Diamond Science and Technology, Washington, D.C. Sept. 23-27, 1990.

- G. -H. M. Ma, B.E. Williams, J.T. Prater and J.T. Glass; " Analysis via Transmission Electron Microscopy of the Quality of Diamond Films Deposited from the Vapor Phase", presented at Diamond Films '90; to be published in Diamond and Related Materials (Elsevier Science), Volume 1, Number 1, August 1991.

- J. A. von Windheim and J.T. Glass; "Improved Uniformity and Selected Area Deposition of Diamond by Oxy-acetylene Flame Method, J. Materials Research, 7 (8), (1992), p. 2144-50.

- M.T. McClure, J. A. von Windheim, J.T. Glass and J.T. Prater; "Early Nucleation of Combustion Flame Diamond", Novel Forms of Carbon, edited by C.L. Renschler, J.J. Pouch and D.M. Cox, MRS Symposium Proceedings Vol 270 (1992), p.323.

- X.H. Wang, W. Zhu, J.A. von Windheim, and J.T. Glass, "Combustion Growth of Large Diamond Crystals, Submitted to J. Cryst. Growth.

- J. A. von Windheim, F. Sivazlian, M.T. McClure, J.T. Glass and J.T. Prater; "Nucleation and Growth of Diamond Using Computer Controlled Oxy-Acetylene Torch", to be presented at the DIAMOND 1992, August 31 - September 4, 1992 in Heidelberg, Germany; and submitted for publication in the Conference Proceedings in Diamond and Related Materials.

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- M.T. McClure, J. A. von Windheim, J.T. Glass and J.T. Prater, "Effect of Native SiO_2 Layer on the Nucleation of Diamond Using a Combustion Flame", submitted to Diamond and Related Materials.

THESES:

- G.-H. M. Ma, Ph.D. Thesis, Microstructural Studies by TEM of Diamond Films , 1991.

- M.T. McClure, Masters Thesis, Effect of Substrate Surface on the Nucleation of Diamond by the Combustion Flame Technique, 1992.

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PATENTS: NONE

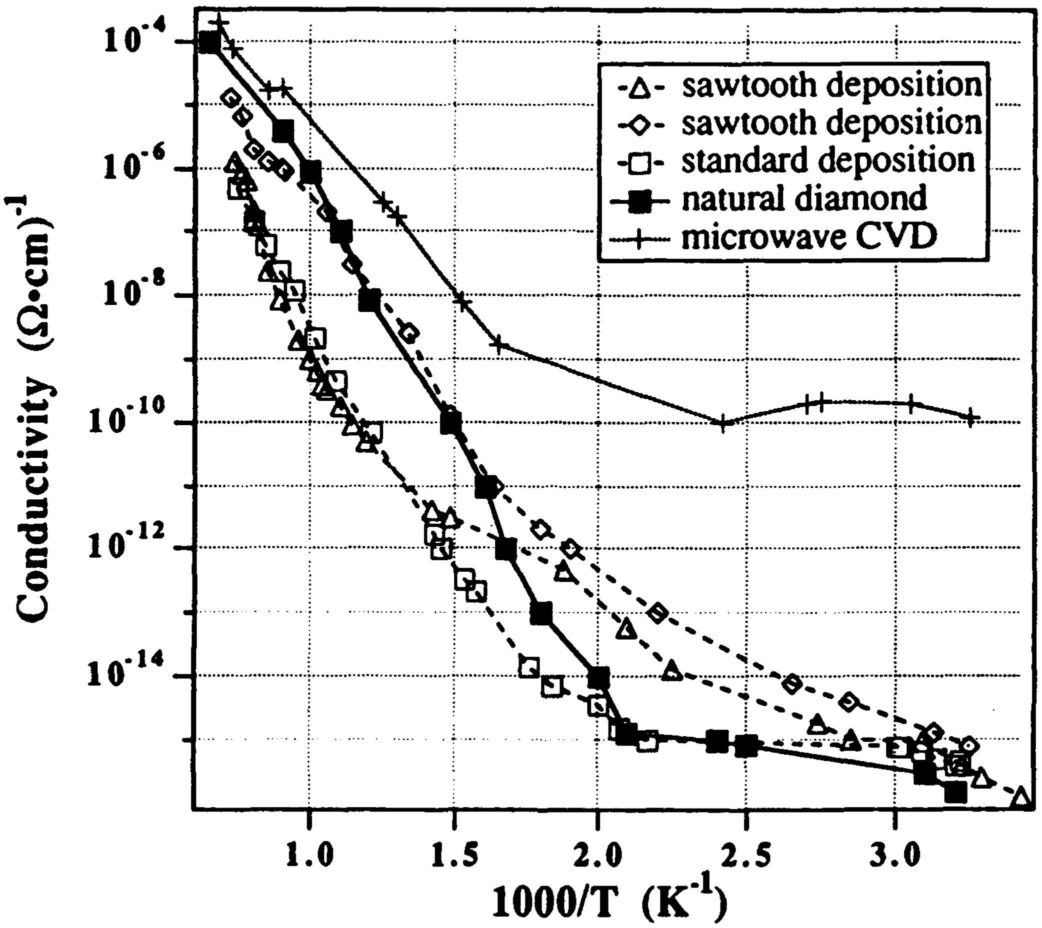


Figure 1. Temperature dependence of conductivity for various diamond samples. The open symbols represent combustion grown films with different acetylene-to-oxygen ratios and deposition/etching sequences.

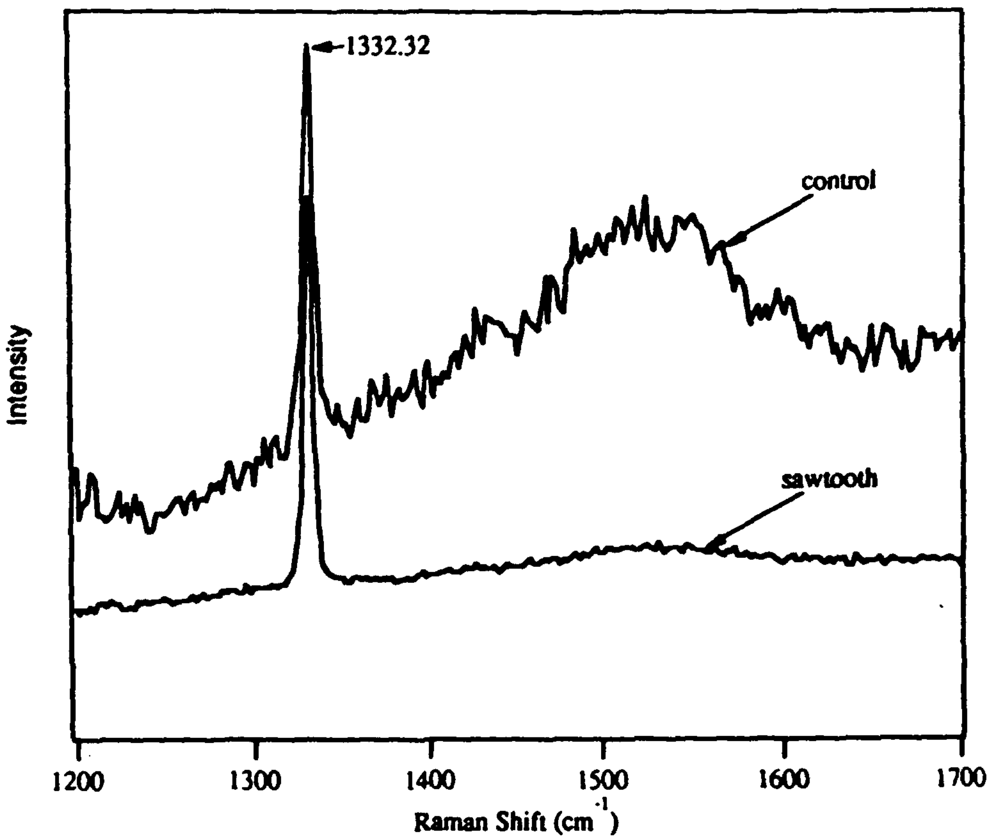
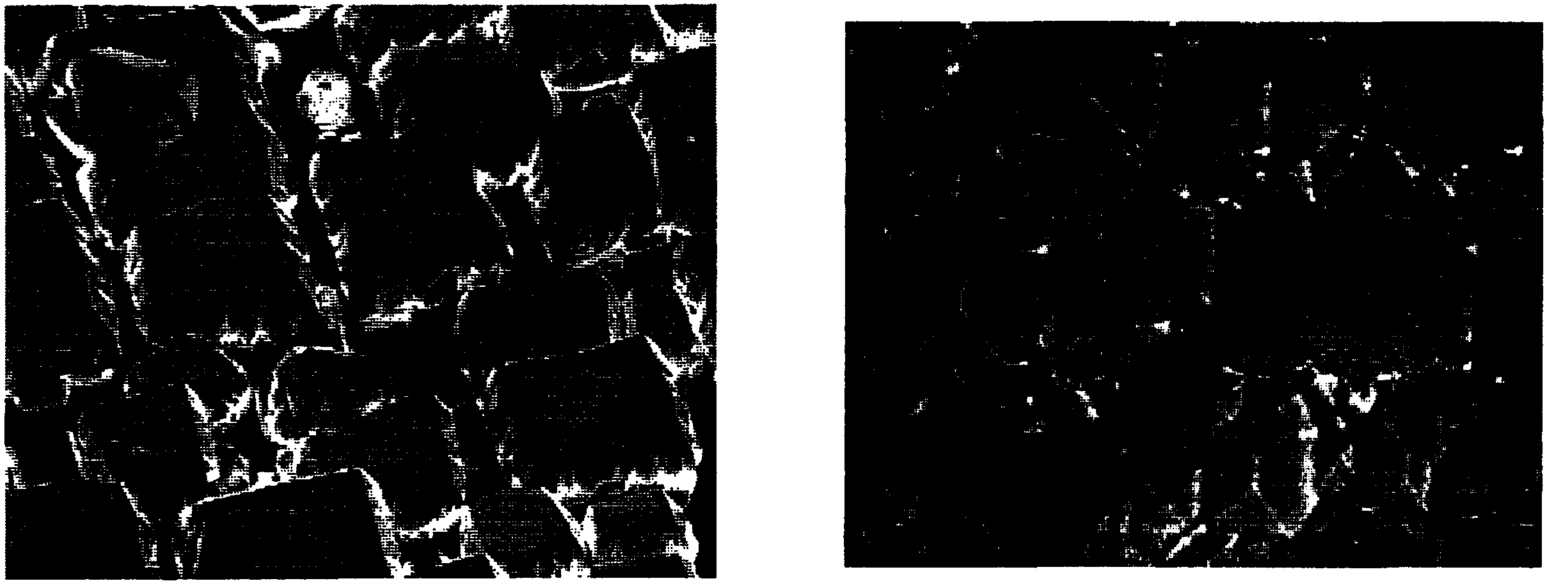


Figure 2. Raman Spectra for two combustion grown diamond films. The lower curve refers to a diamond film grown were the flame chemistry was periodically altered to introduce oxygen-rich (etching) conditions.



a) 250 µm b) 2.5 µm

Figure 3. Nearly continuous, highly textured diamond films have been grown by combustion flame on Si(100) substrates pretreated to provide well oriented diamond seeds: a) mosaic substrate provided by M. Geis (1) at Lincoln Labs, and b) microwave pretreated substrate prepared at North Carolina State University.

APPENDIX I - ABSTRACTS OF PROGRAM PUBLICATIONS:

PUBLICATIONS:

- G. -H. M. Ma, Y. Hirose, S. Amanuma, M. McClure, J.T. Prater and J.T. Glass; "Microstructural Studies by TEM of Diamond Films Grown by Combustion Flame", accepted for publication in the Proceedings of the 2nd International Conference on New Diamond Science and Technology, Washington, D.C. Sept. 23-27, 1990.

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- M.T. McClure, Masters Thesis, Effect of Substrate Surface on the Nucleation of Diamond by the Combustion Flame Technique, 1992.

MICROSTRUCTURAL STUDIES BY TEM OF DIAMOND FILMS GROWN BY COMBUSTION FLAME

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ABSTRACT

Microstructures of diamond films grown in an oxygen-acetylene combustion flame were studied by Transmission Electron Microscopy (TEM). The O_2/C_2H_2 gas ratio was fixed and the substrate materials and temperature were varied. High quality diamond films were grown by this method at high growth rates of about 30 µm/hr. A rough surface and high density of secondary nucleation sites and microtwins were observed in the diamond grains grown on molybdenum (Mo) at a substrate temperature of 500 °C. When the substrate temperature was raised to between 600 and 870 °C, the defect density was greatly reduced, revealing a low density of stacking faults and dislocations. Near the edge of the diamonds films grown on Mo at 700 °C, numerous microtwins were still observed probably indicating a lower growth temperature due to a temperature gradient across the sample surface and flame. Diamond films grown on Si substrates did not show the same substrate temperature dependence on defect density, at least not over the same temperature range. However, the same correlation between defect density, secondary nucleation, and surface morphology was observed.

INTRODUCTION

Low pressure vapor phase growth of diamond at reasonable growth rates was first demonstrated in 1981.[1] Since then vapor phase synthesis of diamond films and particles has been achieved by at least 10 different methods.[2] Atmospheric growth of diamond on foreign substrates in an oxygen-acetylene combustion flame was first demonstrated by Hirose et a˙[3] This unexpected finding attracted immediate attention and was readily confirmed by Hanssen, et al.[4] and Snail, et al.[5] Due to the simplicity of the approach, the relatively high growth rate and inexpensive equipment requirements, diamond researchers worldwide have been motivated to study this combustion growth technique in detail.[6-11] High quality films with good optical transparency and a sharp Raman 1332 cm^{-1} peak have now been deposited.[12] Research, to date, indicates that the characteristics (morphology, graphitic component) of the diamond films or particles synthesized by oxy-acetylene combustion flames depends on several important parameters, including O_2/C_2H_2 ratio (R), substrate temperature (T_S), and substrate-to-torch distance. High quality diamond has been found to form only in a narrow region of R and T_S.[6,10,11]

No detailed microstructural studies have been reported on diamond formed in a combustion flame, although nearly defect free high quality diamond grains have been confirmed by Transmission Electron Microscopy (TEM).[13] The present study reports on the microstructures that form in diamond prepared by this method,

Analysis via transmission electron microscopy of the quality of diamond films deposited from the vapor phase*

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Abstract

The quality of diamond films deposited from the vapor phase was analyzed via transmission electron microscopy. Diamond films grown by different deposition processes and under various conditions were examined and the processing-microstructure relationships were established. Defect structures are first reviewed here. Twinning was the predominant defect observed in all of the diamond samples, but stacking faults and dislocations were also found. It was found that a lower methane concentration resulted in a lower defect density (higher quality) in diamond films grown by microwave-plasma-enhanced chemical vapor deposition. The defect density in diamond films was also reduced if reverse bias was applied in a bias-controlled hot-filament chemical vapor deposition system, in contrast with the high defect density which occurred under the forward bias condition. Finally, the imperfection density was substantially reduced if diamond films were grown at higher substrate temperatures in an oxyacetylene torch.

1. Introduction

Diamond possesses a unique combination of highly favorable technological properties, such as high hardness, strength, thermal conductivity, electron-saturated drift velocity, hole and electron mobilities, chemical and thermal stability, radiation hardness and optical transparency [1, 2]. Currently, intensive research activities around the world are aimed at developing a new era in diamond technology which will fully utilize these unique properties of diamond in applications ranging from coatings for wear resistance and cutting tools to optical windows for visible and infrared (IR) transmission, as well as thin films for high temperature, high power semiconductor devices. Substantial progress has been made in this field and currently diamond film and particle synthesis from the vapor phase under low pressure is routinely achieved by more than 10 different methods. However, although epitaxial diamond films can be grown on diamond substrates [3-5], for diamond to reach its true potential, high quality monocrystalline films must be grown on economically viable non-diamond substrates. Judging from

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#249 Flame CVD Diamond

Improved uniformity and selected area deposition of diamond by the oxy-acetylene flame method

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(Received 27 September 1991; accepted 30 March 1992)

The role of SiO_2 in nucleation of diamond has been investigated in an oxy-acetylene flame. It was found that growth methods that minimize SiO_2 formation enhance diamond nucleation. A short pretreatment of a scratched Si surface in a low oxygen-to-acetylene ratio flame, at a distance 1.5 cm from the flame core, significantly improved uniformity of subsequent diamond growth. When scratched surfaces were intentionally oxidized, nucleation of diamond was completely inhibited. By using a mask to controllably deposit SiO_2 on a scratched Si surface, highly selective deposition of diamond was achieved with resolution below 5 μm. These results are discussed with reference to competing oxidation and carbon formation processes that take place during the nucleation of diamond. During the nucleation stage, carbon may be deposited on the scratched Si via a route in which the Si surface catalyzes carbon formation reactions that are otherwise kinetically unfavorable. The formation of an oxide layer, on the other hand, would act to passivate the surface, and thus inhibit carbon formation via a catalytic route. The decomposition of CO to C and CO_2 is given as an example of a reaction that is favored at temperatures below 1000 K, but requires surface catalysis to proceed because it remains frozen out in the gas phase due to a very slow reaction rate.

NTRODUCTION

Since the growth of diamond by oxy-acetylene torch ; first reported by Hirose,[1] a significant amount work has focused on understanding the flame mistry[2-5] as well as growth dynamics[6] in order to prove the uniformity of diamond films. While a high sity, annular ring of diamond forms at the perimeter the flame, a significant problem has been the lack growth in the central region of the flame front.[3-5] It been suggested that a large radial variation in flame mistry may be responsible for these observations.[3,5] ious strategies have been employed to minimize this uniformity. Oaks *et al.*[5] found that growth was more form when the substrate was moved 6 mm from the ne core; they concluded that concentrations of flame cies were more homogeneous in this region of the ne. Others have improved uniformity by growing mond with the substrate at an angle relative to the me direction. For instance, Tzeng *et al.*[7] grew at a 70° gle relative to the flame to obtain complete films on Si. wever, it seems that in those cases where uniform diamond films were achieved, growth had to be preceded by ow oxygen-to-acetylene ratio (R_f) pretreatment. Thus, vi *et al.*[8] used a short, low R_f pretreatment to significantly improve film coherence, whereas Tzeng *et al.*[7] o reported a low R_f (0.85) pretreatment to be necessary their work at large angles relative to the flame.

In this report the deposition of pinhole-free diamond films on Si, over the entire flame, front is described. A key factor in obtaining these films was a pretreatment that was carried out at 1.5 cm from the flame core. This was followed by growth at 1.5 mm from the flame core. Both pretreatment and growth took place with the substrate surface directly perpendicular to the flame direction. By applying the pretreatment to Si substrates masked off with SiO_2, highly selective growth over relatively large areas has been achieved with an oxy-acetylene flame.

The experimental setup consisted of a standard welding torch with a #2 tip. The oxygen and acetylene flow rates through the torch were controlled by MKS mass flow controllers (MFC), and the total flow for both gases was typically 4000 sccm. Substrate temperature was regulated by a water cooled copper stage, and substrate surface temperature was measured by a two-color pyrometer (Williamson 8220). Both the MFCs and the pyrometer were interfaced to a PC via a Keithley/Metrabyte DASCON1 DAC/ADC board. A QuickBasic program was written to monitor and control the growth so that complicated gas profiles could be programmed and run without supervision, and gas flow and temperature could be continuously monitored. An example of an $O_2:C_2H_2$ ratio profile and a substrate temperature profile, measured during a typical

EARLY NUCLEATION OF DIAMOND IN A COMBUSTION FLAME, Michael T. McClure, Jesko A. von Windheim, and Jeffrey T. Glass, North Carolina State University, Raleigh, NC; and John T. Prater, Army Research Office, Research Triangle Park, NC

Abstract

The early stages of a gas phase pretreatment for diamond nucleation in an oxy-acetylene flame were investigated. The pretreatment involved a low oxygen-to-acetylene ratio (R_f) performed at 15 mm from the torch on a scratched Si substrate. The nature of the carbon species deposited was analyzed using X-ray photoelectron spectroscopy, scanning Auger electron spectroscopy, and scanning electron microscopy. 180 seconds of the pretreatment process produced a complete film in the center of the deposition area and the first diamond crystals appearing after 30 seconds. Furthermore, the pretreatment process kept the oxide layer less than the thickness generated by the control conditions, ($R_f = 0.93$, d = 15mm). The success of the pretreatment was attributed to changes in the flame structure and chemistry from the control conditions.

Introduction

The invention of the combustion flame diamond synthesis technique by Hirose in 1988[1] generated considerable interest in the field of diamond research because of its low start up cost and high growth rate. However, a disadvantage is that the diamond growth has been limited to an annular ring when the flame direction is normal to the substrate.[2, 3] To circumvent this problem, researchers have tilted the flame relative to the substrate[4] and/or used a low gas ratio pretreatment step[5, 6] before operating under normal growth conditions.

When the low O_2:C_2H_2 ratio (R_f) pretreatment step was used, the researchers found an increase in the nucleation density leading to continuous film deposition even in the center of the flame front.[5, 6] One explanation given[5] for the success of the pretreatment involved the deposition of a diamond-like carbon layer, which was speculated to provide a higher concentration of hydrogen in the growth region and to be a highly defected structure providing a large number of nucleation sites. Alternatively, Windheim and Glass[6] suggested that the pretreatment step primarily suppresses oxide formation on the substrate surface and allows frozen equilibrium reactions to continue.

Because high nucleation density and film growth throughout the flame front are important for improved efficiency and future scale-up of the

Combustion Growth of Large Diamond Crystals

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Abstract

This paper reports the successful growth of optically transparent, individual diamond crystals up to millimeter diameters on silicon substrates by oxygen-acetylene combustion flames at atmospheric pressure. The growth process consisted of three steps; (i) achieve a suitable nucleation density by pretreating the as-received Si substrate in an acetylene-rich flame (oxygen-to-acetylene ratio $R_f = 0.95$) for about 30 minutes at a downstream position (7-10 mm away from the tip of the flame inner cone); (ii) grow crystals up to ~200 microns in diameter in an annular area on the substrate at $R_f = 0.98$ and a substrate-to-tip of the flame inner cone distance of 2 mm; and (iii) move the preferred crystals from the annular region into either the central core region of the flame feather or near the edge of the flame feather for further growth up to millimeter diameters under carefully controlled conditions. The final step of moving the crystals into a different growth region was necessary to avoid extensive secondary nucleation and structural defects. The key factor for diamond crystals to grow up to millimeter diameters was to maintain the growth conditions at the growing surface constant throughout the process. It was found that the crystal surface temperature, which was the most sensitive and also one of the most critical parameters, could be

effectively maintained constant by decreasing the total gas flow rate as growth continued. Both the crystal growth orientations and the amount of nitrogen impurity incorporated in the diamond lattice were closely related to the crystal surface temperature. It is believed that the gas flow dynamics, or more specifically, the boundary layer thickness, played an important role in the growth and morphological development of large diamond crystals.

For Reveiw Purposes Only (printed November 2, 1992)

To be presented at Diamond '92, Heidelberg, Germany (for publication in DRM)

Nucleation and Growth of Diamond Using a Computer Controlled Oxy-Acetylene Torch

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Abstract

A computer controlled oxy-acetylene torch was used to nucleate and grow polycrystalline diamond films. The computer interface was designed to continuously monitor and/or modify oxygen and acetylene flow rates, while a PID temperature controller was used to stabilize the substrate temperature at selected set points. This system significantly enhanced the control and reproducibility of the diamond growth, leading to increased area (50 mm^2), high quality diamond films.

A pretreatment was used to enhance the nucleation of diamond. This pretreatment involved an oxygen-to-acetylene ratio of 0.93-0.95, with the substrate ~15 mm from the torch nozzle. Surface analysis revealed that diamond was deposited in as little as 30 seconds, with a significant amount of carbon being incorporated in the sp^2 form. When the substrate was subsequently moved up into the flame, and the oxygen-to-acetylene ratio was increased, good quality diamond was observed to deposit on the pretreated area, over the entire area of the flame front.

Utilizing computer control, systematic and complex variations in gas chemistry could be applied during growth. Thus the oxygen-to-acetylene ratio was modified between 0.97 and 1.01 using a saw tooth function, resulting in larger grain sizes relative to normal growth conditions, with very little sp^2 bonding.

Submitted to: Phys. Rev. B15, July 8, 1992

Examination of the Diamond and Beta-Silicon Carbide Heteroepitaxial Interface

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Abstract

A comparative study of both theoretical and experimental aspects of the diamond/beta-silicon carbide (β-SiC) heteroepitaxial interface was performed. The theoretical modelling was conducted to examine the various combinations of like and unlike interfacial planes between diamond and β-SiC based on a geometric criterion formulated in reciprocal space for minimization of interfacial misfit and strain energies. The modelling results indicated that the low index unlike pair between diamond {114} and β-SiC {221} has the greatest potential for minimizing the interfacial energy and is, therefore, strongly recommended for experimental investigations. The low index like pairs between diamond and β-SiC are next in

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potential, and diamond(001)/β-SiC(001) heteroepitaxy has been confirmed via experimental observations. Other configurations yield high interfacial energies and are unlikely to occur. The relatively high strain energy associated with the like pair heteroepitaxy can be relieved by the introduction of misfit dislocations at the interface. These misfit dislocations have also been experimentally observed by cross-sectional transmission electron microscopy. The calculated misfit dislocation densities correlate well with the experimental measurements. The misfit dislocations observed in diamond not only accommodate the misfit strain but also cause both interfacial tilting and azimuthal rotational misorientations.

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EFFECT OF NATIVE SiO_2 LAYER ON THE NUCLEATION OF DIAMOND USING A COMBUSTION FLAME

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ABSTRACT

The effect of native oxide thickness on the nucleation of diamond was investigated. The initial thickness of the native oxide on Si substrates was varied using three surface treatment methods: ultrasonic scratching, HF acid etching, and a combination of the two. The oxide layer was also modified during the experiment by using a low O_2:C_2H_2 ratio pretreatment (R_f = 0.93, d = 15 mm). The use of HF acid eliminated the oxide layer within the detectable limits of the XPS analysis (≈3Å). A low gas ratio pretreatment process (oxygen-to-acetylene ratio, R_f, set to 0.93) diamond crystals were formed after 30 seconds and a complete film in the center of the deposition area after 180 seconds. The low gas ratio pretreatment suppressed the formation of the oxide layer relative to standard growth conditions (R_f = 0.97, d = 10 mm). However, it was determined that despite this low gas ratio pretreatment SiO_2 formation was possible inside the acetylene feather.

1. INTRODUCTION

To make diamond thin films applicable to a wide variety of technologies, understanding the nucleation process is essential. In particular, high nucleation densities are necessary for uniform polycrystalline films and single crystal films.

MICROSTRUCTURAL CHARACTERIZATION OF DIAMOND FILMS

by

GUANG-HWA MIKE MA

A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Doctor of Philosophy

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

Raleigh

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Chair of Advisory Committee

Abstract

MA, GUANG-HWA MIKE. Microstructural Characterization of Diamond Films (Under the direction of Dr. Jeffrey T. Glass).

Powerful microstructural characterization techniques have been utilized to investigate three important issues for diamond films prepared from the vapor phase under low pressure. These issues include; (a) establishing microstructure-processing relationships and the understanding of defect formation mechanism, (b) understanding nucleation processes, (c) evaluating titanium contact formation mechanisms.

From this study, it has been demonstrated that defect densities will be affected and controlled through variations in processing parameters. Microstructure-processing relationships established include; (1) Forward biasing in a hot filament chemical vapor deposition (CVD) creates a high density of defects. (2) Gas species in microwave plasma enhanced CVD has a significant impact on the microstructures of diamond films. Both boron doping and oxygen addition into the gas phase have been shown to enhance the quality of diamond films. (3) In the temperatures range studied (500 - 900 °C), high substrate temperature facilitate the growth of diamond films with low defect densities in the combustion flame technique. Detailed discussions of possible mechanisms reponsible for these microstructural changes have also been given.

All of these results also suggested that twins and stacking faults in vapor deposited diamond were created when a deposition error arising on the {111} planes during the growth. In addition, the full width half maximum of

the diamond Raman peak was found to correlate very well with the defect density.

Regarding the nucleation studies, the diamond scratching pretreatment, know to enhance diamond nucleation, created a highly defected and contaminated substrate surface prior to the diamond growth. A carbonaceous phase was found between the diamond films and the substrate in the diamond films grown under various substrate pretreatment conditions. A two stage surface evolution model, which involves a surface carbonaceous layer favorable for diamond nucleation, was developed and discussed.

Ti/diamond interfaces were also examined in this study. Detailed microstructural characterization revealed that the state of this interface determined the contact characteristics. When the interface between titanium and diamond was modified, it caused various changes in the contact characteristics.

EFFECT OF SUBSTRATE SURFACE ON THE NUCLEATION OF DIAMOND BY THE COMBUSTION FLAME TECHNIQUE

by

MICHAEL THOMAS MCCLURE

A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the requirements for the Degree of
Master of Science

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Raleigh

1992

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Chair of Advisory Committee

Abstract

MCCLURE, MICHAEL THOMAS. Effect of Substrate Surface on the Nucleation of Diamond by the Combustion Flame Technique (Under the direction of Dr. Jeffrey T. Glass).

Deposition of diamond thin films is desirable to lend diamond's excellent properties to a variety of technologies. Diamond's high strength and hardness and low coefficient of friction make it an ideal candidate for wear and cutting applications. Its index of refraction, transparency in a wide range of frequencies, and chemical and radiation inertness are well suited as a window material in a harsh environment. However, many applications require a uniform film or a single crystal film. To achieve these types of films requires controlling and understanding the nucleation of diamond. Among the many methods to enhance the nucleation of diamond, abrading or scratching the surface is the most common. To date, the exact function of the scratches have not yet been determined.

This research investigates the proposed role of scratches by examining surface roughness, oxide thickness, and carbon contamination surface treatment methods. Increasing surface roughness and reducing oxide thickness resulted in enhanced diamond nucleation. The addition of butanol and hexane to the surface prior to growth repeatedly resulted in diamond deposition. Individually, however, none of these surface treatments resulted in particle densities equal to the scratched samples. A gas phase pretreatment was also used to investigate the competing roles of oxide formation and diamond formation, as well as being another method for saturation of the surface with carbon. Those experiments revealed that high quality growth conditions were not ideal for high nucleation.

The same experiments also illustrated how gas condition can nullify surface treatment methods.

This research determined that oxide formation was a competitive surface reaction for diamond nucleation. Carbide formation was another competitor, but was not evident in this system. To achieve the highest possible nucleation density of diamond, surface treatments and gas conditions must favor diamond formation and suppress competitive reactions.